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Natural minerals as oxygen carriers for chemical looping combustion in a dual circulating fluidized bed system

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Abstract

A first experimental campaign has been conducted at a 120 kW fuel power dual circulating fluidized bed installation for chemical looping combustion of gaseous fuels. In these test runs natural ilmenite ($FeTiO_3$) has been used as oxygen carrier material. The plant consists of two interconnected circulating fluidized bed reactors (stainless steel construction, inner diameter: 0.15 m, height: air reactor 4.1 m, fuel reactor 3 m). Variations of fuel composition (natural gas, synthetic gas mixtures of H_2 and CO), load, temperature and solids circulation rate have been performed for the bulk bed material. Further, natural olivine, $(Fe,Mg)_2SiO_4$, has been studied as an additive to increase hydrocarbon conversion. Despite the limited height of the risers, the results show reasonable fuel conversion for CO and H_2 at 950°C. The conversion of natural gas, i:e. CH_4, on the other hand, is relatively low for the pure ilmenite material at about 30-40%. A certain dependency of fuel conversion on load is found especially for CH_4. Addition of natural olivine results in a moderate increase of CH_4 conversion.

Keywords: Carbon capture, Unmixed combustion, Chemical looping, Oxygen carriers, Ilmenite, Olivine, Dual fluidized bed

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1. Introduction

Chemical looping combustion (CLC) is a novel combustion process that avoids direct mixing of fuel and combustion air. The CLC technology uses metal oxide particles for selective oxygen transport from the air reactor to the fuel reactor, thus pure CO_2 is obtained in the fuel reactor exhaust stream after condensation of water without further gas separation needed. The process features 100% carbon capture rates, a highly concentrated stream of CO_2 ready for sequestration, no NO_x emissions [1], and no costs or energy penalties for gas separation. CLC uses well-established boiler technology very similar to circulating fluidized bed boilers, which also means that costs can be assessed with great accuracy. CLC is estimated to achieve significant CO_2 capture cost reductions compared to today's best available technology, namely post combustion amine scrubbing [2].

The major challenge with CLC is the availability of adequate oxygen carriers. The requirements for a good oxygen carrier are high oxygen transport capacity, high reactivity, high mechanical strength and low production costs [3]. Typically, these requirements are best achieved if the active metal oxide is provided on a ceramic support structure with a high surface area. Such designed particles can be produced using different methods. A wide range of different oxide/support combinations have been selected and studied in recent years [4]. From thermodynamics point of view, the interesting redox systems for CLC are CuO/Cu, CoO/Co, Fe_2O_3/Fe_3O, Mn_3O_4/MnO_4 and NiO/Ni, as well as a number of perovskites. Cobalt and nickel based carriers show thermodynamic limitations with respect to full conversion of CO and H_2, but they are very reactive towards hydrocarbons on the other hand. The other carriers thermodynamically allow full fuel conversion to CO_2 and H_2O, but their reactivity is lower on the other hand. Further, Fe, Mn, Co and Cu can take in more than two oxidation states. However, not all of these are relevant for CLC.

Ilmenite, a natural iron-containing mineral, has been proposed as cheap and readily available oxygen carrier for CLC of solid fuels [5]. Ilmenite is conventionally used as a raw material for TiO_2 pigment production. Some processes for ilmenite upgrading and Fe/Ti separation for pigment production involve oxidation and subsequent reduction of ilmenite. The solid phase chemistry of ilmenite in different oxidation states has been studied by different authors [6,7]. In the raw mineral, most of the iron is present as Fe_{II}.in $FeTiO_3$ (ilmenite phase). According to Nell [7], essentially two solid solution phases may occur if ilmenite is increasingly oxidized. The first region is represented by the ilmenite structure M_2O_3, where $TiFeO_3$ (Fe_{II}) and and Fe_2O_3 (Fe_{III}) are miscible within certain limits. Along with oxidation, rutile (TiO_2) is formed according to:

$$2\ FeTiO_3 + 0.5\ O_2 \rightarrow Fe_2O_3 + 2\ TiO_2 \qquad (1)$$

Rutile crystallites have been found outside of the M_2O_3 structure. At the same time, free cation sites are generated in the M_2O_3 structure due to the addition of anion (oxygen) sites. Electrical effects make the electron donating iron atoms move to the crystal surface [7].

If oxidation proceeds further, a second phase with a M_3O_5 structure appears. Again, there is a certain miscibility reported between $FeTi_2O_5$ (pseudobrookite = Fe_{II}) and Fe_2TiO_5 (ferric pseudobrookite = Fe_{III}). And again rutile is formed along with oxidation:

$$2\ FeTi_2O_5 + 0.5\ O_2 \rightarrow Fe_2TiO_5 + 3\ TiO_2 \qquad (2)$$

Despite the fact that rutile is formed and appears outside of the iron-containing phases the original ilmenite phase is re-formed during reduction of oxidized material. This is described for the Murso process [8] where the raw material is first oxidized to M_3O_5 phases (with TiO_2 formed) and subsequently converted back to $FeTiO_3$ in a reduction roasting. This implies that the rutile moves back in the original structure during reduction.

Leion et al. [9] have tested cyclic stability of ilmenite during repeated cycles of oxidation and reduction and found an increase in reactivity with increasing cycle number during the first 10-20 cycles. After that, the reactivity in terms of CO conversion has remained constant. It seems that ilmenite is a serious candidate for a cheap and environmentally sound oxygen carrier in chemical looping combustion. However, the reactivity towards methane is low for iron-based carriers, what turns into a problem for CH_4 rich fuels like natural gas.

Olivine, $(Fe,Mg)_2SiO_4$, is applied as bed material in fluidized bed biomass gasification and some moderate catalytic activity towards hydrocarbon reforming has been reported [10]. In the present study, olivine is used as an additive to ilmenite in some experiments with the intention to improve methane conversion.

2. Bulk reactions and definitions

Generally, in the fuel reactor, the gaseous fuel species CO, H_2 and CH_4 may be oxidized in contact with the solid oxygen carrier. In the following expressions, the ilmenite chemistry is lumped into the formal expressions FeO (Fe_{II}) and Fe_2O_3 (Fe_{III}), even though iron seems to always appear in combination with TiO_2 if ilmenite is the raw material.

$$CO + Fe_2O_3 \rightarrow CO_2 + 2\ FeO \qquad (3)$$

$$H_2 + Fe_2O_3 \rightarrow H_2O + 2\ FeO \qquad (4)$$

$$C_xH_y + (2x + 0.5y)\ Fe_2O_3 \rightarrow x\ CO_2 + 0.5y\ H_2O + (4x + y)\ FeO \qquad (5)$$

In parallel to the oxidation Reactions (3)-(5), CO and H_2 may be formed from hydrocarbons. This happens due to partially incomplete progress of Step (5) or via reforming of hydrocarbons. A detailed investigation of the complex chemical reaction mechanisms involved in hydrocarbon conversion in the fuel reactor would exceed the scope of the present effort. Instead, some basic definitions are made in the following to quantify experimental observations.

The conversion of a fuel species is generally defined as

$$X_i = 1 - \frac{\dot{n}_{FRout} \cdot y_{i,FRout}}{\dot{n}_{FRin} \cdot y_{i,FRin}}. \qquad (6)$$

In chemical looping combustion, where the focus is on high fuel conversion to CO_2, the CO_2 yield from the fuel reactor is defined according to

$$\gamma_{CO_2} = \frac{\dot{n}_{FRout} \cdot y_{CO_2,FRout}}{\dot{n}_{FRin} \cdot \sum_i \left(\xi_{C,i} \cdot y_{i,FRin}\right)}. \qquad (7)$$

3. Experimental

A dual circulating fluidized bed test rig has been designed and built with hot commissioning in January 2008. The main design data are 120 kW fuel power natural gas and a global air ratio of 1.0…1.2. The design of the unit is discussed into detail elsewhere [11]. The air reactor (AR) of the CLC system is designed as fast fluidized bed determining the global solids circulation rate. The fuel reactor (FR) is designed as a second circulating fluidized bed reactor with the return loop of the entrained solids into itself. The FR may be optimized with respect to gas phase conversion. The lower loop seal connecting the two reactors represents a continuation of the reactor bodies and closes the global circulation loop. The main fluidization nozzles are arranged along the circumference of the cylindrical reactor shells. A sketch of the test rig with the most important geometric data is shown in Figure 1.

The fuel reactor may be supplied with either natural gas or with synthetic gas mixtures from gas cylinder stacks (H_2, N_2, CO). Fuel and air volume flows to the reactor system are continuously registered and controlled using rotary flow meters and control valves. Temperature and system pressure is taken at 30 positions at the test rig. In order to remove the heat released from combustion and to control the system temperature independently of the global air ratio, the air reactor shell is equipped with cooling jackets. These cooling jackets are operated either with boiling water or gaseous cooling media. The cyclone separators are designed according to Hugi [12]. The loop seals are fluidized with steam in nominal operation and may be switched to air fluidization during start-up and shut-down. The exhaust gas streams of the two reactors are cooled separately to about 573 K and analyzed on-line (Rosemount

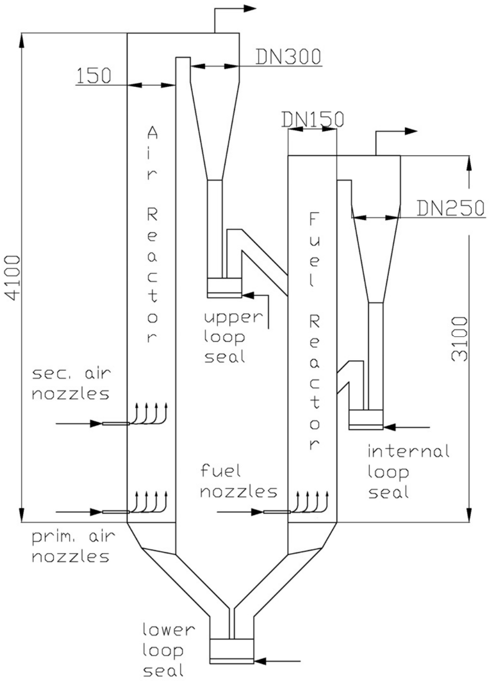


Figure 1: Sketch of the test rig designed for 120 kW natural gas operation.

Species	wt.%
TiO_2	44.08
Fe^{2+}	25.93
Fe^{3+}	9.14
O with Fe	11.36
P_2O_5	0.03
S	0.14
Cr_2O_3	0.08
SiO_2	3.10
CaO	0.42
MgO	4.38
Al_2O_3	0.93
MnO	0.29
K_2O	0.04
Na_2O	0.10
Sum	100.00

Table 1: Chemical composition of the ilmenite used based on data supplied by Titania A/S.

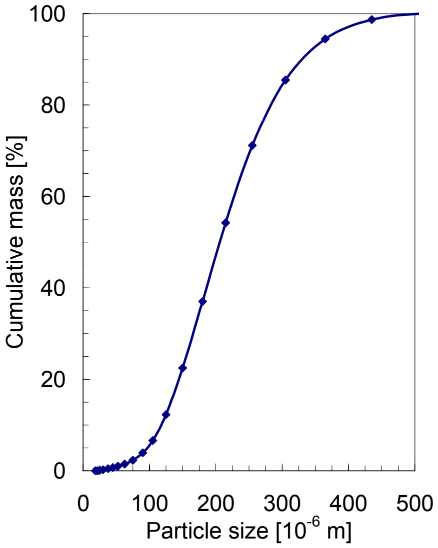


Figure 2: Size distribution of the ilmenite used.

NGA 2000) to evaluate the conversion of the fuel as well as the leakages of the loop seals. The cooled exhaust gas streams pass valves. These allow for imposing defined backpressure on each reactor. The exhaust gas streams are then mixed and sent to a natural gas fired post combustion unit, cooled again, filtered and sent to the chimney. The whole laboratory plant is monitored and controlled using a commercial process control system.

In a first experimental campaign directly after hot commissioning, ilmenite has been used as oxygen carrier material. The chemical composition and the size distribution of the ilmenite used are reported in Table 1 and Figure 2, respectively.

Due to defluidization problems when working with fresh ilmenite in chemical looping conditions, an oxidative pre-treatment of the ilmenite for 3-6 h at 850 °C has been performed at the installation before switching to chemical looping operation. This procedure solves the defluidization problem effectively. Each experimental run has lasted between 12 and 16 hours in total. Different operating points have been run during each day of experimentation. For natural gas operation, natural olivine has been tested as an additive to ilmenite. Table 2 reports the ranges of operating parameters during this first test campaign at the pilot rig with ilmenite as the bulk bed material.

Due to several difficulties at the beginning, only limited power ranges have been run for syngas mixtures. Fuel addition to the air reactor has been necessary in most cases to keep the system temperature. However, some basic results for natural minerals as oxygen carriers in CLC of gaseous fuels can be reported. The performance data can be compared to the data of designed NiO-based oxygen carriers tested in a later campaign and reported at this conference [13].

Parameter	Unit	Fuels		
		$H_2 + N_2$	$H_2 + CO$	natural gas
Fuel power	kW	24 - 43	40 - 92	20 - 130
Temperature air reactor	°C	895 - 978	887 - 983	813 - 986
Temperature fuel reactor	°C	894 - 966	878 - 976	839 - 969
Content of O_2 in air reactor exhaust	v-%(dry)	8.5 - 11.0	9.3 - 14.2	3.6 - 12.8
Total mass ilmenite	kg	70 - 90	70 - 85	70 - 90
Total mass additive (olivine)	kg	0	0	0 - 15

Table 2: Ranges of operating parameters during ilmenite runs.

4. Results and discussion

A key towards the interpretation of results is a general picture of the fluid dynamics of the system. Figure 3 shows the pressure profile of the system measured at 120 kW operation with ilmenite. An exponential decay of pressure is found in the air reactor. This is typical for circulating fluidized bed risers and indicates the decrease of solids concentration with height. The FR on the other hand, shows a concentration of solids in the bottom region, indicated by the steep pressure change between positions FR 1 and FR 2 (Figure 3). The upper regions of the fuel reactor are, therefore, very lean in solids and no real circulating regime is reached in this case for the fuel reactor. The reasons for the limited development of the circulating regime are lower gas velocities due to limited fuel conversion and increased mean particle size of the solids. In comparison, the system has been designed for a mean particle diameter of 0.120 mm and full fuel conversion has been assumed for the design case [11].

The fuel conversion for CO and H_2 is shown versus fuel power in Figure 4 for a 1:1 mixture of CO and H_2 as fuel. The results mirror the apparent reactivity of the system. A slight decrease of fuel conversion is found with increasing load. This indicates that the gas-solids contact time, which decreases with increasing load, governs the fuel reactor performance in this case. Taking the non-optimal fluid dynamic situation in the fuel reactor into account, it can be assumed that there is room for improvement of syngas conversion rates in the future. Combustion of CO and H_2 plays an essential role in the context of CLC for solid fuels.

Figure 5 shows the CH_4 conversion and the CO_2 yield versus fuel power with natural gas as fuel in the fuel reactor. The CH_4 conversion is generally relatively low in these runs. A high dependency of fuel reactor performance on load is witnessed. A change of the global solids inventory from 70 kg to 85 kg shows little effect.

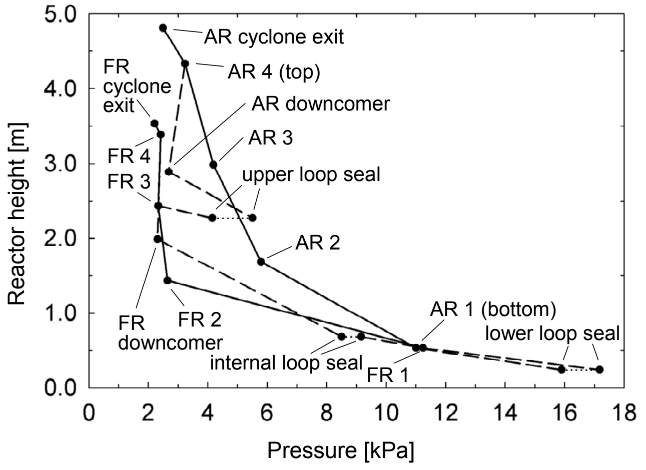


Figure 3: Pressure profile in the reactor system with ilmenite at 120 kW operation with natural gas.

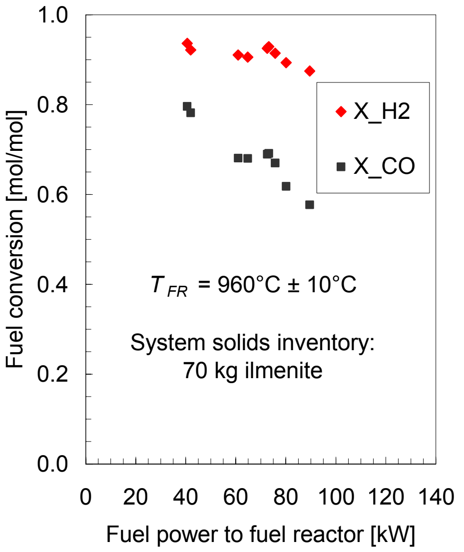
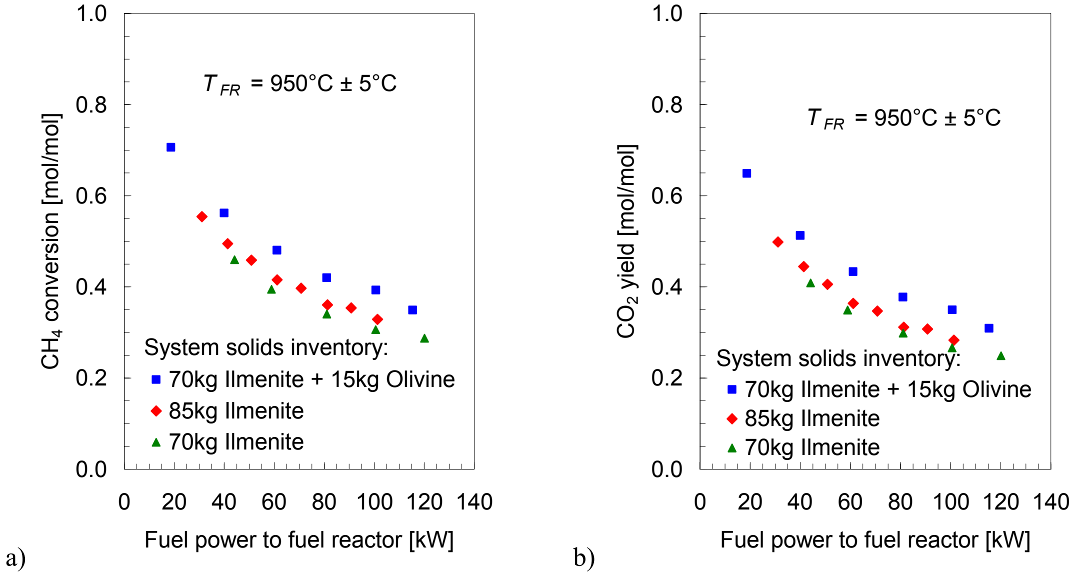


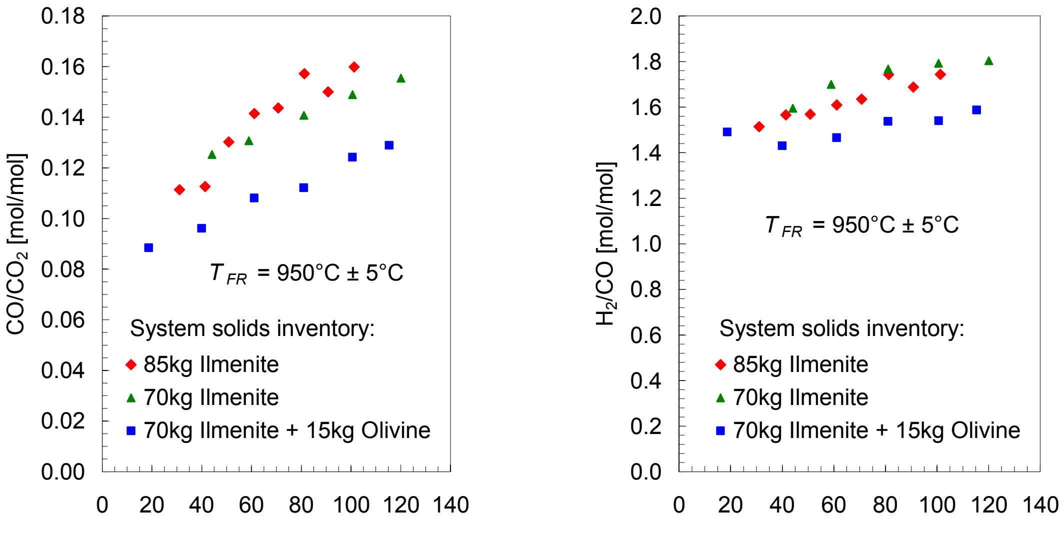
Figure 4: Fuel conversion in the fuel reactor for syngas operation (CO:H_2 = 1:1).



a) b)

Figure 5: Fuel conversion (a) and CO_2 yield (b) for 100% natural gas operation with different solids inventories.

An interesting aspect is that the 85 kg run where about 18% of the bed material have been replaced by natural olivine shows some improvement in CH_4 conversion. Again, the results indicate that the reactivity in the fuel reactor limits the system performance. The amount of CO and H_2 leaving the fuel reactor can be derived from the CO/CO_2 ratio and from the H_2/CO ratio shown in Figure 6. It turns out that the slip of the uncombusted species CO and H_2 through the fuel reactor is slightly increasing with increasing load and, therefore, with increasing hydrocarbon slip. Olivine addition shows some effect on the fuel reactor exhaust stream and slightly reduces CO as well as H_2. All in all, also these results for natural gas conversion own some potential for future improvement. It is expected that with fluidized bed riser reactors of adequate height (12-18 m) and reasonable fluidizing velocities for solids distribution over the whole height, significantly better fuel conversion rates can be achieved.



a) b)

Figure 6: Ratio CO/CO_2 (a) and ratio H_2/CO in fuel reactor exhaust gas for natural gas operation with different solids inventories.

5. Conclusions

A first experimental campaign has been performed on a novel dual circulating fluidized bed system for chemical looping combustion using natural ilmenite as bed material. The system has been designed for 120 kW fuel power natural gas operation with NiO-based oxygen carriers. Several conditions have still not been optimized during these first runs using ilmenite. Coarser particles and lower gas flow rates compared to the design case caused a non-optimal solids distribution in the fuel reactor. Nevertheless, reasonable fuel conversion between 60 and 90 % has been found for syngas (CO and H_2), which is the main product of coal gasification. The operation with natural gas shows moderate conversion of CH_4 and a strong dependency on load. Partial replacement of ilmenite by natural olivine improves the hydrocarbon conversion moderately. In conclusion, combinations of natural minerals offer some potential as cheap and environmentally sound oxygen carriers, especially for fuels with low gaseous hydrocarbon contents like gasification product gas or solid fuels. It is important to mention that the results have been obtained from a pilot plant and the performance of the oxygen carriers reported needs to be regarded as the performance of the carrier in this specific system at the parameters operated. The chemistry of ilmenite during repeated cycles of oxidation and reduction will certainly require more attention in the future.

6. Acknowledgement

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The ilmenite used in the experiments has been supplied by Titania A/S, Norway.

7. Notation

T	temperature	°C
X_i	conversion of species i	mol·mol^{-1}
y	gas phase mole fraction	mol·mol^{-1}
γ_{CO2}	CO_2 yield based on carbon supplied	mol·mol^{-1}
$\xi_{C,i}$	number of carbon atoms in molecule of species i	mol·mol^{-1}

Super-/Subscripts

AR	air reactor
FR	fuel reactor
i	reference to gas species
in	gas stream into reactor
out	gas stream from reactor

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